Competitive Formation of Polymer−Cyclodextrin Inclusion Compounds

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ABSTRACT: The hydrophobicity of the guest polymer and also the geometrical compatibility between guest polymer cross section and cavity diameter of the host cyclodextrin (CD) play important roles in the formation of inclusion compounds (ICs) between a mixture of one or two guest polymers with one or two different types of CDs, respectively. Specific polymer−CD interactions can be distinguished when, for example, polymer A−CD IC crystals are suspended in a solution containing polymer B, and a polymer B for polymer A exchange occurs, without CD−IC dissolution, during formation of polymer B−CD IC. When using the polymer pair poly(ϵ-caprolactone) (PCL)/poly(L-lactic acid) (PLLA), we have observed that PLLA−α-CD IC is completely converted to PCL−α-CD IC, while the reverse polymer transfer is almost completely prohibited. α-CD host molecules also preferentially included PCL chains from a common PCL/PLLA solution. In addition, observation of the transfer of PCL from PCL−γ-CD IC crystals suspended in a solution containing α-CD to form PCL−α-CD IC crystals now suspended in a solution containing γ-CD, while not observing the reverse transfer, has implications for the relative strength of polymer ↔ polymer and polymer ↔ CD interactions. Single and pairs of side-by-side parallel PCL chains occupy the channels of PCL−α-CD IC and PCL−γ-CD IC crystals, respectively, so our observations suggest that interactions between included PCL chains, which are only possible in PCL−γ-CD IC, do not lead to an increased stability for polymer−CD ICs.

Introduction

Many studies have been conducted to understand the natures of the forces driving cyclodextrin inclusion compound (CD IC) formation and the importance of noncovalent interactions in supramolecular chemistry.[1−5] Nonetheless, the driving forces important for complexation, especially for polymer−CD IC formation, are still unclear and controversial.

The most used host molecules in supramolecular chemistry are cyclodextrins, mainly because of their structures and inclusion properties, which make them different from other host molecules, like crown ethers, urea, thiourea, perhydrotriphenylene, or calixarenes.[6] Cyclodextrins represent a series of cyclic oligosaccharides consisting of six to eight glucose units, called α-, β-, and γ-CD, respectively. Because of their shallow truncated cone shape, they can act as host molecules including both polar and nonpolar molecules as well as small or long molecule guests. Guest molecule types and experimental conditions lead to the packing of the host CD molecules in one of two principal modes, described as cage and channel structures, in their IC crystals. When a small molecule is included in the cavity of the host CD molecules, a “herringbone” arrangement, with both ends of one CD cavity blocked by adjacent CDs, is obtained for IC crystals. A channel-type structure is characteristic for long-chain molecule guest−CD ICs. The channel or columnar CD crystal structure, without included guests aside from water of hydration, can be readily obtained by an appropriate recrystallization process from a suitable solvent[7] or by removing the included, threaded polymers from polymer−CD IC crystals under the action of a selective organic solvent.[8,9] Thus, the channel structure consisting of endless columns of stacked CD molecules connected to each other by hydrogen bonds has proved to be a stable structure even when there are no guest molecules included other than water.

Host cyclodextrin molecules generally possess a greater inclusion affinity for more hydrophobic, rather than hydrophilic, guest polymers. To confirm this, here we attempted an interchange transfer between PCL chains in solution and guest PLLA chains in its α-CD IC crystalline powder without dissolution of the IC structure. The analytical results (X-ray diffraction, FTIR spectroscopy, and differential scanning calorimetry (DSC)) obtained for the resulting powder indicate that the α-CD IC retains its initial channel structure but contains only guest PCL chains. An attempt at a reverse transfer reveals that only a small amount of the initial PCL guest chains in its α-CD IC were replaced by PLLA chains in solution. Moreover, when the α-CD IC was obtained from a common solution of PLLA/PCL, the host α-CD molecules preferred to include only the PCL chains.

Furthermore, we were able to demonstrate that guest−host steric compatibility plays an important role in the formation of one specific polymer−CD inclusion compound. Starting with a 1:1:1 molar ratio of α-CD:γ-CD:PCL in solution (enough PCL to form α-CD IC, $^1/_2\gamma$-CD IC, or a mixture of the two ICs), PCL was forced to choose between the two available host molecules. The filtered white powder proved to be a channel structure of α-CD IC, with PCL chains included in its host channels. The observed transfer of PCL chains from PCL−γ-CD IC crystals to uncomplexed α-CD in solution led to the same conclusion. The unsuccessful reverse transfer of PCL from PCL−α-CD IC to free γ-CD evidenced the fact that PCL chains show a strong affinity for the smaller cavity of α-CD.

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Experimental Section

Materials. α-CD and γ-CD were obtained from Cerestar (Hammond, IN). 1,4-Dioxane (99+%) and acetone (99.9+%) were purchased from Aldrich and were used without any further purification. Poly(ϵ-caprolactone) (M_w = 65 000) and poly(L-lactic acid) (M_w = 285 000) were obtained from Aldrich and Polyscience, Inc., respectively.

Preparation of Samples. *PCL−α-CD/γ-CD IC Formation*. 3.625 g of α-CD and 5.8 g of γ-CD were dissolved in 50 mL of deionized water in order to obtain a saturated CDs aqueous solution at room temperature. Meanwhile, 0.399 g of PCL was dissolved in 150 mL of acetone at 50 °C. The heated (50 °C) CDs solution was then added dropwise to the polymer solution also maintained at 50 °C. The resulting white suspension was stirred at 50 °C for 3 h and then allowed to cool to room temperature, while continuously stirring overnight. A white powder was collected by vacuum filtration and then washed several times with cold water and acetone to remove the uncomplexed CD and free PCL, respectively.

Transfer of PCL from Its γ (α)-CD IC to Free α (γ)-CD. A suspension of 1 g of PCL−γ-CD IC in 25 mL of acetone (1 g of PCL−α-CD IC in 10 mL of acetone) at room temperature was slowly added to the aqueous saturated α (γ)-CD solution, which consisted of 1.5 g of α-CD in 10.3 mL of deionized water (or 1 g of γ-CD dissolved in 4.4 mL of deionized water). The final suspension was heated at 55 °C and stirred overnight. The next day, the resultant crystalline powder was vacuum-filtered and washed repeatedly with cold water and acetone.

Interchange between PLLA (PCL) Chains in Solution and PCL (PLLA) Chains in Its α-CD IC Channels. 0.07 g of PLLA (0.05 g of PCL) was dissolved in 25 mL of dioxane at 50 °C. 0.5 g of PCL (PLLA)−α-CD IC powder was suspended in the polymer solution and continuously stirred at 50 °C for 60 h. At the end of this period, the IC powder was separated by vacuum filtration and washed with dioxane to remove any free polymer.

α-CD IC Formation from a PLLA/PCL Polymer Solution. 0.5 g of PLLA and 0.4 g of PCL were both dissolved in 150 mL of dioxane at 80 °C. The polymer solution temperature was then reduced to 60 °C. While the polymers dissolved, 3.625 g of α-CD was combined with 25 mL of deionized water in a flask submerged in a 60 °C oil bath. The aqueous α-CD solution was then added to the PLLA/PCL solution via a pipette. This solution was continuously stirred overnight at 60 °C. The vacuum-filtered powder was washed with dioxane.

Finally, all the above CD IC powders were dried in the vacuum oven at 50 °C for 24 h. Formation and characterization of PCL−α-CD IC, PCL−γ-CD IC, and PLLA−α-CD IC were previously reported.[10,11]

Characterization. *Wide-Angle X-ray Diffraction.* Wide-angle X-ray diffraction (WAXD) measurements were performed on a Siemens type-F X-ray diffractometer with a Ni-filtered Cu Kα radiation source ($\lambda = 1.54$ Å) The supplied voltage and current were 30 kV and 20 mA, respectively. The diffraction intensities were measured every 0.1° from $2\theta = 5°$ to 30° at a rate of ($2\theta = 3°$)/min.

Differential Scanning Calorimetry. DSC measurements were carried out on 3−5 mg samples with a Perkin-Elmer DSC-7 thermal analyzer equipped with a cooler system. A heating rate of 10 °C/min was employed, and indium and tin standards were used for calibration. Nitrogen at 20 mL/min was used as the purge gas.

Fourier Transform Infrared Spectroscopy. A Nicolet 510P FT IR spectrometer was utilized to obtain the infrared spectra of samples mixed into potassium bromide and pressed into pellets. The spectra were recorded over the range of 4000−400 cm^{-1}, with a resolution of 2 cm^{-1} using 64 scans.

Thermogravimetric Analysis. TGA scans were obtained with a Perkin-Elmer Pyris 1 thermogravimetric analyzer on 5−10 mg samples. Samples were placed in an open platinum pan that was hung in the furnace. The weight percentage of remaining material in the pan was recorded during heating from 25 to 550 °C at a heating rate of 20 °C/min. Nitrogen was used as the purge gas.

Results and Discussion

The CD ICs described in this paper were first analyzed by DSC in order to make certain that the polymer(s) used in the IC preparation is (are) completely included. It is well-known that as long as the potential guest is included in the CD IC channels, no endothermic peak related to the fusion of the crystalline bulk phase of the guest is exhibited in the corresponding DSC thermogram. When a polymer−CD IC is successfully obtained, the included polymer chains are completely segregated by host matrix walls and thus are not able to associate to form crystals. Consequently, all of the CD IC powders were tested by DSC between room temperature and 200 °C, a temperature range where the host CD molecules do not show any thermal events. Absence of endothermic peaks corresponding to the fusion of crystalline PCL (60 °C) and/or PLLA (164 °C) in all related IC thermograms indicated that the CD IC samples did not contain any free polymer(s). Moreover, TGA measurements of all CD ICs (not shown here) proved that the polymer guests included in the CD channels improve the thermal stability of the host CD molecules, which showed higher decomposition temperatures (>320 °C) than uncomplexed CDs.

Before assessing the importance of hydrophobic interactions and steric compatibility between the CD hosts and guest polymers investigated here, we first need to carefully examine the structures of the resultant PCL−α-CD, PCL−γ-CD, and PLLA−α-CD ICs. The characterization of α (γ)-CD IC crystal structures by wide-angle X-ray diffraction is described in our or other previous reports.[12−17] The most intense diffraction peak at $2\theta \cong 20°$ in the α-CD IC patterns has been identified as a fingerprint for the channel (or columnar) structure of α-CD. Also, the strongest peak at $2\theta = 7.5°$ seen in the diffraction patterns of γ-CD IC powders is well-known to be characteristic for its channel crystal structure.

The FTIR spectra of pure CD, as-received PCL, PCL−α-CD IC, PCL−γ-CD IC, as-received PLLA, and PLLA−α-CD IC are presented in Figure 1. Both α-CD and γ-CD show similar FTIR spectra, having their most characteristic absorption bands at 1026 and 1079 cm^{-1} due to coupled C−C/C−O stretching vibrations and 1158 cm^{-1} attributed to the asymmetric stretching vibration of the C−O−C glycosidic bridge.[18] Since CD vibrational bands cover most of the IR spectrum between 400 and 4000 cm^{-1}, the strong carbonyl stretching bands of the guest polyesters are the clearest observable and diagnostic peaks in their CD IC samples. Strong peaks at 1736 and 1758 cm^{-1}, corresponding to the stretching of the carbonyl groups in PCL and PLLA, are evident in the spectra of PCL−α-CD IC, PCL−γ-CD IC, and PLLA−α-CD IC, respectively. The presence of bands characteristic for the carbonyl groups and glycosidic bridges in the IC spectra demonstrates that both the polymers and host CD molecules are present in the ICs. This analytical evidence alone does not say anything about where the guest polymer chains are located. However, after combining the above information with that provided by DSC and WAXD, we may conclude that all of the ICs have been successfully formed, their channel structures were built through strong hydrogen bonds between the hydroxyl groups of neighboring CDs, and

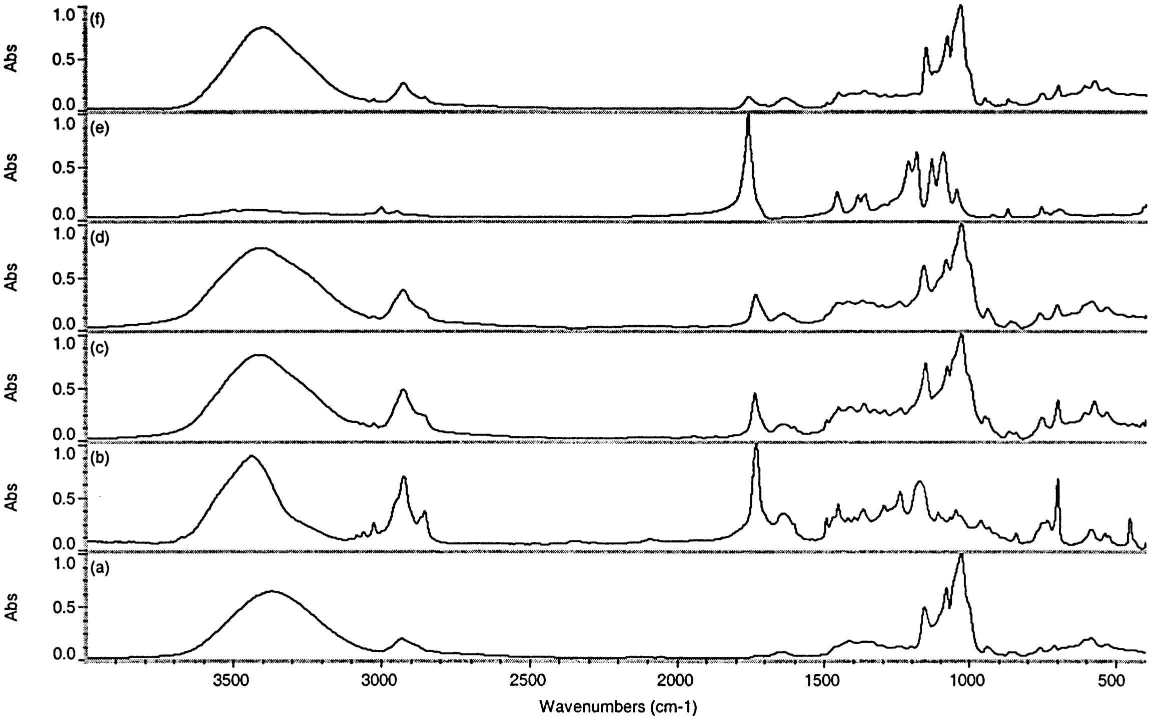

Figure 1. FTIR spectra of (a) pure CD, (b) as-received PCL, (c) PCL−α-CD IC, (d) PCL−γ-CD IC, (e) as-received PLLA, and (f) PLLA−α-CD IC.

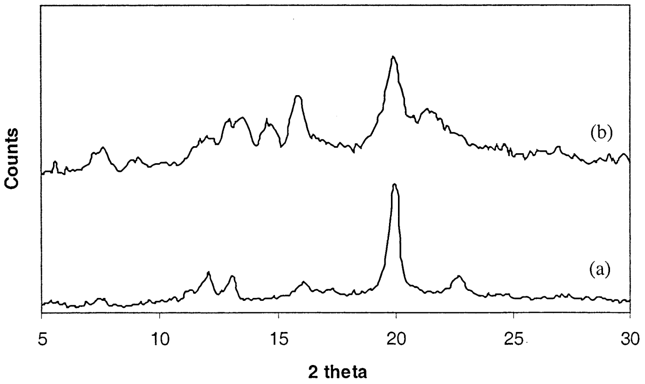

Figure 2. Comparison of the X-ray patterns recorded for (a) PCL−α-CD/γ-CD IC crystals (1:1:1 molar ratio) and (b) PCL−α-CD IC/PCL−γ-CD IC physical mixture (1:1 weight ratio).

the channels are fully occupied by the guest polyester chains.

Competition between α-CD and γ-CD for PCL. Starting with a 1:1:1 molar ratio of α-CD:γ-CD:PCL in solution, PCL chains were forced to choose between the two available host molecules. As we know from our previous studies,[10,11] the host−guest stoichiometric ratios are 1:1 for PCL−α-CD IC and 2:1 for PCL−γ-CD IC. Consequently, a 1:1:1 molar ratio of α-CD:γ-CD:PCL represents enough PCL to form either α-CD IC, $^1/_2\gamma$-CD IC, or a mixture of the two ICs from their common solution.

The X-ray diffraction patterns of the CD IC obtained from α-CD:γ-CD:PCL (1:1:1 molar ratio) and a PCL−α-CD IC/PCL−γ-CD IC physical mixture (1:1 weight ratio) are shown in Figure 2. The more complicated pattern obtained for the IC physical mixture of PCL−α-CD IC/PCL−γ-CD IC attests to the fact that the former IC does not contain both IC crystals. The X-ray diffractogram of PCL−α-CD/γ-CD IC shows diffraction peaks at $2\theta = 7.8°$, 12.2°, 13.2°, 16.3°, 20°, and 22.9° that are attributable solely to the channel structure arrangement of α-CD molecules and does not represent a superposition of α-CD and γ-CD in cage or channel structures. Though not shown, the FTIR spectrum and DSC thermogram of PCL−α (γ)-CD IC clearly demonstrate that the PCL component is present in this IC sample in an included state. Although γ-CD may form an IC with two parallel PCL chains, included side by side in the same channel,[11] the PCL chains preferentially thread the tighter (4.5 Å) and apparently more appropriate host cavity, rather than the larger γ-CD cavity (8.5 Å), resulting in a PCL−α-CD IC. Two possible scenarios may be envisaged. In the first, both α-CD IC and γ-CD IC may be formed from PCL chains dissolved in the common solution at the beginning of the crystallization process, and then a transfer of guest PCL chains from γ-CD IC channels to the remaining free α-CD molecules in solution may occur. This is supported by further experiments described below. The second scenario is related to the difference between the two inclusion rates, where a higher rate of PCL inclusion into α-CD vs γ-CD biases the entire crystallization process toward formation of PCL−α-CD IC.

The greater affinity of PCL chains for the α-CD host, rather than γ-CD molecules, was also noted when PCL was extracted from its CD IC channels using a selective solvent for the guest polymer, which is a nonsolvent for CD. Using the same solvent (acetone) and temperature (50 °C), PCL was completely removed from its γ-CD IC channels after 24 h, whereas the PCL−α-CD IC crystals still contained guest polymer after 5 days of extraction. The presence or absence of PCL in its CD ICs was verified by FTIR spectroscopy (not shown). While the C=O absorption peak of the guest PCL chains cannot be seen in the acetone-washed γ-CD IC spectrum, the C=O absorption peak of the remaining included PCL chains at 1736 cm^{-1} is only a bit smaller than the C=O peak intensity in the initial PCL−α-CD IC spectrum. This experiment proves that any hydrogen-bonded network formed between host and guest molecules is

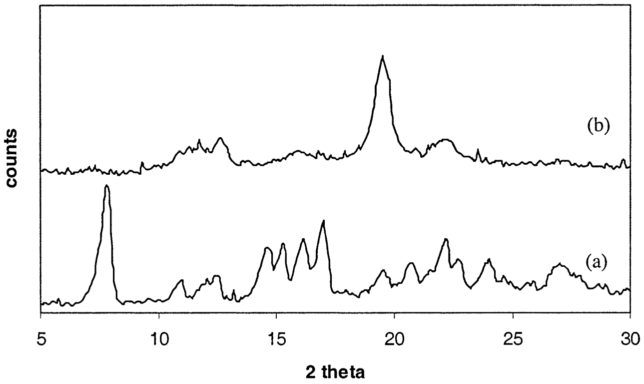

Figure 3. X-ray diffractogram patterns of the IC crystals (a) before and (b) after PCL chains transfer from its γ-CD IC to free α-CD.

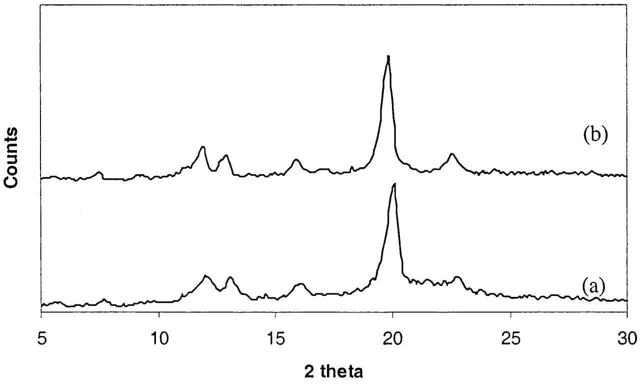

Figure 4. X-ray diffractogram patterns of the IC crystals (a) before and (b) after PCL chains transfer from its α-CD IC to free γ-CD.

stronger in PCL−α-CD IC than in PCL−γ-CD IC, possibly because of parallel, side-by-side inclusion of PCL chains in the PCL−γ-CD IC, which would restrict these host−guest interactions.

Transfer of PCL Chains from Its γ-CD IC to Free α-CD. A mixture of an aqueous saturated α-CD solution with a suspension of PCL−γ-CD IC in acetone was stirred for 15 h at 55 °C. The amount of α-CD was calculated to be stoichiometric for the entire amount of PCL that could be potentially unthreaded from its initial γ-CD IC.

X-ray diffractogram patterns of the initial and final IC powders are displayed in Figure 3. The X-ray diffractogram in Figure 3a is characteristic for γ-CD IC in the channel structure, where we clearly notice the sharp peak at $2\theta = 7.5°$, whereas the pattern of the powder collected after exposure to dissolved α-CD (Figure 3b) is different and similar to the diffractogram of α-CD IC in a channel structure. For both IC powders, no peaks corresponding to the crystalline phase of the uncomplexed PCL are detected. This indicates that PCL chains reside exclusively in the channels of both the starting and resulting IC crystals, which is consistent with their DSC scans (not shown) recorded between 25 and 100 °C. The presence of the included PCL chains in both IC samples is confirmed by FTIR spectroscopy. Therefore, we may conclude that a transfer of PCL chains from PCL−γ-CD IC channels to the uncomplexed α-CD molecules took place in the acetone/water solvent system at 55 °C. The driving force(s) critical to the transfer of PCL chains remain unknown, and additional experiments may be needed to understand this transfer phenomenon.

The unsuccessful reverse transfer of PCL chains from PCL−α-CD IC to free γ-CD in solution provides further evidence that PCL macromolecules show a stronger affinity for the smaller cavity of α-CD. In this experiment the necessary stoichiometric amount of γ-CD in deionized water was mixed with a suspension of PCL−α-CD IC in acetone for 15 h at 55 °C. As can be seen in Figures 3 and 4, using exactly the same conditions (time, temperature, and solvent system), the resulting PCL−CD IC structure is similar irrespective of whether we start with PCL−α-CD or PCL−γ-CD ICs. The PCL−α-CD IC channel structure, proved by the intense diffraction peak at $2\theta = 20°$ for the resulting powder, is not surprising if this result is considered in light of the other experiments described above. The presence of included PCL chains in the PCL−α-CD IC powder was determined by FTIR spectroscopy. Lack of a PCL melting peak in the DSC thermogram (not shown) and no diffraction peaks due to the crystalline phase of PCL in the WAXD pattern of PCL−α-CD IC indicate that the IC sample is free of uncomplexed PCL.

Interchange between Polymer 1 in Solution and Guest Polymer 2 in Its α-CD IC. The following set of experiments suggests a greater inclusion affinity of CD molecules for more hydrophobic guest polymers, rather than hydrophilic ones, when the host CD is forced to form an IC from a mixture of two different guest polymers. As we have previously demonstrated,[19] the host α-CD exhibits molecular weight selective polymer inclusion in the complexation process. α-CD preferentially includes, though not exclusively as urea, high molecular weight poly(ethylene glycol) (PEG) from a common solution of two different molecular weight PEGs. Therefore, we thought that it might be interesting to investigate what happens when the host CD molecules are faced with a choice between two guest polymers with different hydrophobicities. For this reason, two polyesters were chosen, namely PCL and PLLA, that can individually form ICs with α-CD.[10] Also, when we attempted to achieve a PCL/PLLA intimately compatible blend by coalescence from their common IC crystals, we succeeded in the simultaneous inclusion of PCL and PLLA chains in the α-CD IC channels.

In contrast with this last experiment, here the amount of α-CD used in the IC formation was sufficient for complexing either all of one or half of each PCL or PLLA guest. A common solution of PCL:PLLA:α-CD (1:2:1 molar ratio) in dioxane/water was used to obtain α-CD IC crystals. The FTIR spectrum of the resulting IC powder (not shown) looks similar to that recorded for PCL−α-CD IC (see Figure 1c). Lack of absorption bands characteristic for PLLA suggests that PCL inclusion in the α-CD IC was favored over PLLA inclusion, even though the PLLA chains ($M_w = 285\,000$) are ~3 times the length of the PCL chains ($M_w = 65\,000$) when both are fully extended. Since the inner cavity of α-CD is nonpolar relative to its outer surface, α-CD molecules would be expected to prefer threading onto the more hydrophobic guest chains in a mixture of two possible guest components. Although the role of the hydrophobic interactions in CD complexation is not completely understood and remains controversial, the fact that most inclusion processes are often accompanied by a large negative heat capacity change indicates that the hydrophobic host ↔ guest interactions are important to their association.[20] Also, the importance of hydrophobic interactions is revealed by the fact that the most

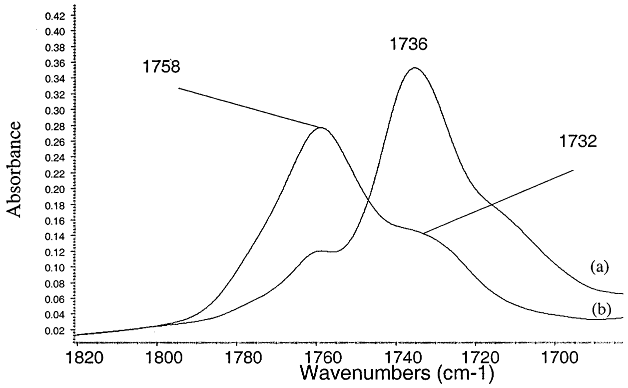

Figure 5. FTIR spectra of (a) the resulting PCL/PLLA−α-CD IC and (b) the precipitated polymer powder collected from the filtered solution.

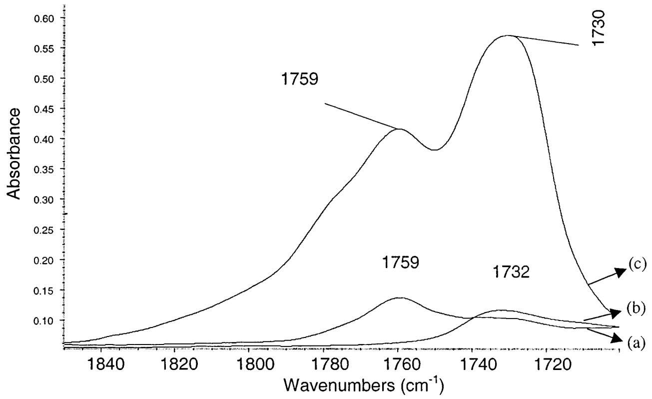

Figure 6. Comparison of FTIR spectra recorded for (a) the initial PLLA−α-CD IC, (b) the resultant α-CD IC, and (c) the precipitated polymer in the filtered solution.

nonpolar portions of the guest molecules are usually included in CD cavities and that the CD can markedly affect the tautomeric equilibrium of the guest molecules by preferentially binding with the less polar tautomer.[21] X-ray diffraction measurements (not shown) reveal a channel structure for the resulting α-CD IC crystals. Also, the DSC thermogram (not shown) was run for this sample, and no endothermic events were found between 25 and 200 °C.

To more closely examine the inclusion affinity of α-CD for more hydrophobic guest polymer chains, we attempted two additional experiments concerning an interchange between two different polymers located outside and inside of their α-CD ICs.

In the first experiment, a previously obtained PCL−α-CD IC powder was suspended in a clear solution of PLLA in dioxane. We should mention that dioxane is a common solvent for both polymers, but a nonsolvent for CD. The stoichiometric amount of PLLA used was enough to replace the entire amount of included PCL. FTIR spectra recorded between 1700 and 1820 cm^{-1} of the resulting α-CD IC and the precipitated polymer powder collected from the filtered solution are presented in Figure 5, while the FTIR spectrum of the starting PCL−α-CD IC is presented in Figure 1c. As can be seen, the α-CD IC crystals resulting after the attempted PLLA/PCL interchange process show both carbonyl stretching bands at 1758 and 1735 cm^{-1} belonging to PLLA and PCL, respectively. Judging from this information, along with the DSC scan of the resulting α-CD IC powder (not shown) that shows no fusion peaks for uncomplexed PCL or PLLA, we may suggest that a small amount of PLLA from the dioxane solution was included into the α-CD IC channels, thereby replacing some of the initially included PCL. During the transfer of polymer chains, the solid α-CD IC crystal structure suffered no modification, as proved by WAXD measurements of the initial and final IC powders involved in this process.

A reverse interchange between PCL in solution and included PLLA chains in its α-CD IC was observed in a second experiment, with identical solvent (dioxane) and experimental conditions. A comparison of FTIR spectra recorded for the initial PLLA−α-CD IC, the resultant α-CD IC, and the precipitated polymer in the filtered solution is displayed in Figure 6. The presence of PLLA in the spectrum (Figure 6a) of its initial α-CD IC is demonstrated by the characteristic band for its carbonyl group at 1759 cm^{-1}, which disappears in the FTIR spectrum of the resulting α-CD IC (Figure 6b), and in this region only an absorption band attributable to the PCL carbonyl group at 1732 cm^{-1} is observed. The entire amount of PCL seen in the FTIR spectrum was determined to be included in the final α-CD IC by means of DSC (not shown). The initial stoichiometric amount of PCL in dioxane solution was calculated to be enough for replacing the entire amount of initially included PLLA. Since the filtered dioxane solution contained both polymers, and not only the extracted PLLA, we may conclude that the entire amount of included PLLA was removed from the initial α-CD IC crystals under the action of dioxane (see Figure 6) but was not replaced by the stoichiometric amount of initially dissolved PCL. Therefore, we can suggest that the channels of the resulting α-CD IC are not fully occupied by the transferred PCL chains.

In an intermediate experiment, α-CD in columnar structure, α-$\mathrm{CD}_{\mathrm{CS}}$, with just a few molecules of water hydrating each α-CD and no other guest included, was suspended in acetone solution containing PCL. As supported by our previous studies on α-$\mathrm{CD}_{\mathrm{CS}}$[7] as well as by Topchieva et al.'s investigations, where CDs in columnar structure were obtained by extracting the threaded polymers from initial polymer−CD IC crystals with a selective organic solvent,[9] we observed inclusion of PCL chains in the α-$\mathrm{CD}_{\mathrm{CS}}$ crystals. X-ray diffraction patterns (not shown) recorded for the initial α-$\mathrm{CD}_{\mathrm{CS}}$ and resulting PCL−α-CD IC show the same unperturbed columnar structure for both of them.

Analysis of Competitive Polymer−CD IC Formation. Let us begin with the complexation of PCL and PLLA with α-CD, where PCL has shown a strong preference compared with PLLA to form PCL−α-CD IC. This preference is observed in the exclusive formation of PCL−α-CD IC from a solution containing both PCL and PLLA and by the transfer of dissolved PCL chains into suspended crystals of PLLA−α-CD IC by displacement of the initially included PLLA chains, without dissolution of the α-CD IC crystals. However, when PCL−α-CD IC crystals were suspended in a solution containing PLLA, very little transfer of PLLA chains and replacement of PCL in the α-CD IC crystals were observed. The latter observations eliminate differences in the kinetics of PCL and PLLA chains threading through and complexing with individual α-CDs as a potential source for the strong preference of PCL chains to form PCL−α-CD IC when in competition with PLLA chains, even though it could have been anticipated[22−24] that PCL chains with cross sections narrower than

PLLA chains might more easily enter and complex with α-CD.

Instead, PCL chains are capable of moving from their solutions and entering the channels of suspended α-CD_{CS} and PLLA−α-CD IC crystals, thereby pushing out and replacing the previously included guest H_2O molecules and PLLA chains, respectively. Clearly then, the interactions and forces between the interiors of the host CD channels and included PCL chains are favorable in comparison to those between the CD channel interiors and included water or PLLA chains. The preference for inclusion of PCL chains over PLLA chains in the channels of α-CD is not a consequence of a greater conformational entropy for the included PCL chains, because both PCL and PLLA are apparently restricted[11,22,23] to their fully extended, all-trans conformations when included in the narrow ~5 Å diameter α-CD channels. Rather, in comparison to PLLA, PCL is more readily included in α-CD because of stronger, more favorable interactions with the interior hydrophobic surface of the host α-CD channels. Because in solution both PCL− and PLLA−α-CD ICs can be formed from their separate α-CD/PCL and α-CD/PLLA solutions, we may additionally conclude that differences between solvent/PCL and solvent/PLLA interactions cannot significantly contribute to the differences observed in their competitive IC formation with α-CD.

We have observed that when dissolved PCL chains are exposed to both dissolved α- and γ-CDs, that only PCL−α-CD IC is formed. In addition, PCL chains may be transferred from the channels of its γ-CD IC crystals to a solution where they complex with dissolved α-CD to form PCL−α-CD IC crystals. The transfer of PCL chains from its α-CD IC crystals to a solution containing dissolved γ-CD to eventually form PCL−γ-CD IC crystals, however, does not occur. If we ignore any potential chemical differences, such as the capability to form host−guest hydrogen bonds, between the interiors of the α- and γ-CD channels, then the difference in the sizes of their channels (~5 Å vs ~8−9 Å, respectively), and where only single and pairs of side-by-side parallel PCL chains are included, respectively, must be responsible for the observed preference in the formation of PCL−α-CD IC compared with PCL−γ-CD IC. Two reasons for the preference of PCL chain inclusion in α-CD can be offered. First, the conformational entropy lost by the PCL chains/CD is approximately twice as large in PCL−γ-CD IC compared to PCL−α-CD IC because of their respective 2/1 and 1/1 PCL/CD stoichiometries. Second, because some of the favorable interactions between included guest PCL chains and the interiors of the CD channels may be replaced by less favorable interactions between the side-by-side PCL chains included in PCL−γ-CD IC, PCL may prefer inclusion in α-CD. However, this does not seem as likely a source for the preferred formation of PCL−α-CD IC because the interior surface area of the γ-CD IC host channel is significantly larger than that of the α-CD IC.

In summary, two main types of competitive IC formation were successfully attempted for the first time. These served to emphasize the role of guest hydrophobicity and guest−host steric compatibility in the formation of certain IC structures from a multiguest solution. Molecular recognition of host CD molecules for a more hydrophobic guest polymer and a guest polymer chain in solution threading and being included in CD molecules with a more suitable cavity diameter have been clearly demonstrated. These two general features of polymer−CD IC formation were further supported by the transfer of PCL chains from PCL−γ-CD IC crystals to free α-CD molecules in solution, which produced PCL−α-CD IC channel structure crystals, as well as by the complete exchange of PLLA chains included in suspended PLLA−α-CD IC crystals by PCL chains initially contained in the suspending solution.

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References and Notes

(1) Lu, L.; Guo, Q. X. *J. Inclusion Phenom.* **2002**, *42*, 1.
(2) Harada, A. *Carbohydr. Polym.* **1997**, *34*, 183.
(3) Harada, A. *Acc. Chem. Res.* **2001**, *34*, 456.
(4) Ceccato, M.; Lo Nostro, P.; Baglioni, P. *Langmuir* **1997**, *13*, 2436.
(5) Okumura, Y.; Ito, K.; Hayakawa, R. *Polym. Adv. Technol.* **2000**, *11*, 815.
(6) Atwood, J. L.; Davies, J. E. D.; MacNicol, D. D. In *Inclusion Compounds*; Academic Press: New York, 1984; Vol. 2.
(7) Rusa, C. C.; Bullions, T. A.; Fox, J.; Probeni, F. E.; Wang, X.; Tonelli, A. E. *Langmuir* **2002**, *18*, 10016.
(8) Topchieva, I. N.; Panova, I. G.; Popova, E. I.; Matukhina, E. V.; Gerasimov, V. I. *Dokl. Chem.* **2001**, *380*, 242.
(9) Topchieva, I. N.; Panova, I. G.; Popova, E. I.; Matukhina, E. V.; Grokhovskaya, T. E.; Spiridonov, V. V.; Gerasimov, V. I. *J. Polym. Sci., Part A* **2002**, *44*, 352.
(10) Rusa, C. C.; Tonelli, A. E. *Macromolecules* **2000**, *33*, 5321.
(11) Lu, J.; Mirau, P.; Tonelli, A. E. *Macromolecules* **2001**, *34*, 3276.
(12) Szejtli, J. *Cyclodextrin and Their Inclusion Compounds*; Academiai Kiado: Budapest, 1982.
(13) Huang, L.; Tonelli, A. E. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1998**, *38*, 781.
(14) Harada, A.; Li, J.; Kamachi, M. *Nature (London)* **1994**, *370*, 126.
(15) Rusa, C. C.; Tonelli, A. E. *Macromolecules* **2001**, *34*, 1318.
(16) Harada, A.; Suzuki, S.; Okada, M.; Kamachi, M. *Macromolecules* **1996**, *29*, 5611.
(17) McDowell, C. C.; Freeman, B. D.; McNeely, G. W.; Haider, M. I.; Hill, A. J. *J. Polym. Sci., Part B: Polym. Phys.* **1998**, *36*, 2981−3000.
(18) Casu, B.; Reggiani, M. *J. Polym. Sci., Polym. Symp.* **1964**, *7*, 171.
(19) Rusa, C. C.; Tonelli, A. E. *Macromolecules* **2000**, *33*, 1813.
(20) Liu, L.; Guo, Q. X. *J. Inclusion Phenom. Macrocyclic Chem.* **2002**, *42*, 1.
(21) Iglesias, E.; Ojea-Cao, V.; Garcia-Rio, L.; Leis, J. R. *J. Org. Chem.* **1999**, *64*, 3954.
(22) Tonelli, A. E. *Macromolecules* **1991**, *24*, 1275.
(23) Tonelli, A. E. *Macromolecules*, **1992**, *25*, 3581.
(24) Shuai, X.; Porbeni, F. E.; Wei, M.; Bullions, T. A.; Tonelli, A. E. *Macromolecules* **2002**, *35*, 3778.

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